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(54) High dielectric constant ceramic material and method of manufacturing the same.

(57) A ceramic material comprising a composition expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$
$0 < d \leq 0.5$
$0 < c+d < 1.0$
$0.3 \leq x \leq 0.65$

having a high dielectric constant (K = 2300 to 7000), a high insulation resistance (CR = 4000 to 18000 ohmF), a low temperature dependence (±10%) to (±22, -33%) upon dielectric constant over a wide

EP 0 257 653 A2

HIGH DIELECTRIC CONSTANT CERAMIC MATERIAL AND METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

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Field of the Invention

The present invention relates to a high dielectric constant ceramic material, and a method of manufacturing the same, and more specifically to a high dielectric constant ceramic material having a small temperature dependence of dielectric constant over a wide temperature range in particular, and the method of manufacturing the same.

Description of the Prior Art

As characteristic items required for dielectric material, there are high dielectric constant, low dielectric constant vs. temperature dependence, low dielectric loss (dissipation factor) small bias voltage dependence of dielectric constant, high capacitance - resistance product, etc.

Among these items, in particular, a sufficiently high capacitance-resistance product (CR product) is required. For instance, Standards of the Electronic Industries Association of Japan prescribes the CR product as high as 500 Mohm.µF at room temperature in the Standards RC-3698B entitled Multilayer Ceramic Chip Capacitors for Electronic Applications. Further, MIL-C-55681 prescribes high CR product values even at high temperature such as 125°C.

Furthermore, stable temperature characteristics (dependence) are required over a wide temperature range. For instance, capacitance change is prescribed as ±15% or less within a temperature range of -55 to +125°C in X7R characteristics in the Standards of Electronic Industries Association (EIA), U. S. A., as shown in Fig. 1.

In the case of multilayer-type elements, since the internal electrode layers and the dielectric layers are sintered simultaneously (cofired) in the form as shown in Fig. 2, it is necessary to use an electrode material stable in the sintering temperature of the dielectric material. Therefore, when the sintering temperature of the dielectric material is high, expensive electrode material as Pt, Pd, etc. should be used. In other words, there exists a need of dielectric material sinterable at relatively low temperature of 1100°C or less so that low-cost material such as Ag is usable as internal electrode material.

In the conventional high dielectric constant ceramic materials, barium titanate ($BaTiO_3$) is generally used as a base material, and stannate, zirconate, titanate, etc. are solid-soluted thereinto.

However, since the sintering temperature of the barium titanate based material is as high as 1300 to 1400°C, high-temperature resistant high-costly material such as platinum or paradium should be used for the internal electrodes, thus resulting in cost augmentation.

To improve the above-mentioned disadvantages involved in barium titanate, various compositions have been developed. For instance, Japanese Published Unexamined (Kokai) Pat. (referred to as JPUP) No. 57-57204 discloses a ceramic dielectric composition mainly composed of lead iron niobate; JPUP No. 55-51759 discloses the one mainly composed of lead magnesium niobate; JPUP. No. 55-144609 discloses the one mainly composed of lead magnesium tungstate; and JPUP No. 58-217462 discloses the one mainly composed of lead magnesium/iron/tungstate.

However, no high dielectric constant ceramic material has so far been obtained such that the dielectric constant is high; the temperature dependence is small over a wide temperature range as -55 to +125°C; the insulation resistance is high; that is, various electric characteristics are excellent and further low temperature sintering is enabled.

On the other hand, some researches have been made to obtain flat temperature characteristics by mixing compositions having different dielectric constant temperature characteristics. For instance, JPUP No. 59-203759 discloses a mixture of $Pb(Mg_{1/3}Nb_{2/3})O_3$ -$Pb(Mn_{1/2}W_{1/2})O_3$ based material, and $Pb(Mg_{1.3}Nb_{2/3}O_3$ -$PbTiO_3$ -$Pb(Fe_{2/3}W_{1/3})O_3$ based material. However, this mixture has large temperature coefficient of dielectric constant (T.C.C.) and is insufficient in temperature characteristics. Further, Japanese Journal of Applied Physics, vol.24(1985)Supplement 24-2, pp.427-429 discloses a mixture of $Pb(Fe_{1/2} Nb_{1/2})O_3$ and $Pb(Fe_{2/3}W_{1/3})O_3$. However, the CR product which is important as a capacitor material is not considered; the T.C.C. thereof is high and the temperature characteristics are insufficient.

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PbO 26.49 to 52.58 wt%
BaO 15.01 to 39.07 wt%
SrO 0.00 to 9.57 wt%
ZnO 0.49 to 6.86 wt%
MgO 0.00 to 3.14 wt%
Nb_2O_5 8.00 to 23.03 wt%
TiO_2 7.81 to 23.39 wt%.

Among these, composition in which part of Ti is substituted with Zr is preferable, because a drop in dielectric constant near the Curie point is small. Therefore, $Ba(Ti_{1-e}Zr_e)$ can be used instead of $BaTiO_3$. In this case, however, the substitution amount of Zr is 6 mol% ($0 \leq e \leq 0.06$) at the most. This is because T.C.C. (temperature coefficient of dielectric constant) increases at high temperature when ceramics composed of the mixed sintered body is formed, if beyond 6 mol%.

Further, when the above composition can be calculated in terms of weight percentage of oxides,

PbO 19.28 to 40.35 wt%
BaO 26.73 to 46.73 wt%
SrO 0.00 to 7.15 wt%
ZnO 0.36 to 5.11 wt%
MgO 0.00 to 2.33 wt%
Nb_2O_5 5.84 to 17.11 wt%
TiO_2 13.08 to 26.64 wt%
ZrO_2 0.00 to 1.93 wt%.

Impurities and additives may be includes as far as the effect of the present invention is not degraded. However, the content of additives such as transition elements, lanthanoid elements of CaO, La_2O_3, MnO_2, CoO, NiO, Sb_2O_3, ZrO_2, and SiO_2 may be 1 wt% at the most.

In manufacturing the multilayer-type element, a binder, a solvent, etc. are mixed with the above-mentioned raw material powder or the mixed and crushed powder to obtain a slurry. The slurry is formed into a green sheet; an internal electrode paste is printed on the green sheet; a predetermined number of sheets are laminated, pressurized and sintered. In the sintering process, since the dielectric material of the present invention can be sintered at low temperature, it is possible to use a low-costly material mainly composed of Ag as the internal electrode material.

Further, since the dielectric material can be sintered at low temperature, it is possible to effectively use this material as a thick film dielectric paste material printed and baked onto a printed circuit board.

The ceramic composition of the present invention is high in dielectric constant and small in temperature coefficient, large in CR product even at high temperature, and therefore excellent in reliability at high temperature.

Further, the bias voltage dependence upon the dielectric constant is excellent as low as 10% or less in 2 kV/mm. Thus, the material of the present invention is usable as dielectric material for high voltage, and further for alternating current circuits and for high frequency circuit, because the dielectric loss (dissipation factor (DF) or tan δ) is quite small.

Since the temperature characteristics of the dielectric constant is excellent, when applied to an electrostrictive element, it is possible to obtain an element having a small temperature dependence relative to displacement.

Further, since the particle size can be arranged uniformly within 0.7 to 3 μm, the breakdown voltage is also high.

The mechanical strength of the material is also excellent as well as the above electric characteristics.

(Examples)

Examples of the high dielectric constant material of the present invention will be described below.

The starting raw materials of $BaCO_3$ and TiO_2 for constituting $BaTiO_3$ are both weighed by a balance so as to form a chemical formula $BaTiO_3$, mixed by a ball mill, calcined at 1000 to 1350°C, and then crushed by the ball mill.

Table 1-a

Sample No.	a (mol%)	b (mol%)	c (mol%)	d (mol%)	x (mol%)
Example 1	0	18	1	19	35
" 2	33	0	1	49	40
" 3	0	5	40	0	40
" 4	0	1	80	0	40
" 5	10	0	50	0	50
Compara. 1	33	0	1	49	40
" 2	33	0	1	49	40
Example 6	0	11	40	20	45
" 7	20	0	0	30	58
" 8	15	5	1	29	58
" 9	20	0	0	30	62
" 10	20	0	0	30	55
" 11	5	15	0	30	55
" 12	20	0	50	45	60
Compara. 3	20	0	0	30	55
" 4	20	0	0	30	55

Table 1-c

Sample No.	P.dia of $BaTiO_3$ (μm)	Dielectric constant K(25°C)	Dielectric loss D.F(%)	CR product 25°C (ΩF)	CR product 125°C (ΩF)	Dielectric C. change rate (%)		
						-55°C	+125°C	Max.
Example 1	1.5	4700	1.2	13000	2900	-22	+9	-22
" 2	1.5	5700	1.1	6500	1900	-21	+5	-25
" 3	1.5	5700	1.2	12000	2600	-21	+9	-21
" 4	1.5	6600	1.0	4600	1200	-32	+8	-32
" 5	1.5	5000	1.1	8800	3300	+1	+20	-21
Compara 1	0.4	3100	0.9	3200	920	+3	-39	-39
" 2	6	5300	1.2	590	320	-19	+11	-33
Example 6	1.5	7200	1.0	17000	3600	-31	+13	-31
" 7	1.5	2730	1.2	9100	3300	-7.0	-3.8	-7.0
" 8	1.5	2610	1.1	13000	5200	-5.9	-9.2	-9.2
" 9	1.5	2620	1.2	8700	2900	-8.1	+0.3	-8.2
" 10	1.5	2920	1.3	9500	3800	-6.4	-4.8	-6.8
" 11	1.5	2640	1.1	16000	6900	-7.2	-1.1	-7.2
" 12	1.5	2810	1.4	11000	4200	-9.2	-2.4	-9.9
Compara 3	0.4	1720	1.0	4600	1120	+3.8	-18.7	-18.7
" 4	6	3500	2.3	890	430	-24.2	+16.1	-24.2

Further, Table 2 shows the test results of Examples 13 to 15 of the composition expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3 \cdot xBa(Ti_{1-e}Zr_e)O_3$$

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Table 2-c

Sample No.	P.dia of $Ba(Ti, Zr)O_3$ (μm)	Dielectric constant K(25°C)	Dielectric loss D.F(%)	CR product 25°C (ΩF)	CR product 125°C (ΩF)	Dielectric C. change rate (%)		
						-55°C	+125°C	Max.
Example 1	1.4	2350	1.2	12000	4500	-3.3	-5.8	-6.1
" 2	1.4	2320	0.9	14000	5800	-5.7	-6.5	-6.8
" 3	1.4	2760	1.1	18000	6500	-6.6	-2.9	-6.6
Compara 5	1.4	2210	1.3	9600	2800	-6.4	-13.9	-13.9

Table 1 indicates that the ceramic composition of the present invention have high dielectric constant (K = 4000 or more) and good temperature characteristics (+22 and -33% or less between -55 and +125°C). Further, the CR product is as large as 5000 ohm.F (25°C) or more, in particular 1000 ohm.F or more even at 125°C, being excellent in reliability at high temperature.

Table 1 indicates that the Comparative Example 1 of $BaTiO_3$ with small particle size has a small dielectric constant and a wide temperature change rate. Further, in the Comparative Example 2 of $BaTiO_3$ with large particle size, the CR product is reduced markedly.

Further, in the Example 6 of $Ba_{0.9}Sr_{0.1}TiO_3$ having a Curie point of about 100°C in place of $BaTiO_3$, excellent characteristics have also been obtained. In addition to the substitution of $BaTiO_3$ with Sr, compositions having a Curie point 10 to 30°C lower due to the substitution of $BaTiO_3$ with Ca, Ce, Zr and Sn have also shown excellent characteristics.

Further, Tables 1 and 2 indicate that Examples 7 to 15 are high in dielectric constant (K=2300 or more) and good in temperature characteristics (within ±10% at -55 to +125°C). Further, in the Examples 13 to 15 using $Ba(Ti_{0.95}Zr_{0.05})O_3$ in place of $BaTiO_3$, in particular, excellent temperature characteristics as ±7.5% or less within temperature range of -55 to +125°C can be obtained. The CR value is also as large as 8000 ohm F (25°C), and further 2500 ohm F or more at 125°C in particular, thus indicating excellent reliability at high temperature.

The Comparative Example 5 is a composition using $Ba(Ti_{0.88}Zr_{0.12})O_3$ in which part of Ti is substituted with 12 mol% Zr in stead of $BaTiO_3$. However, the change rate of the dielectric constant exceeds ±10% at high temperature. Therefore, it is preferable that the substitution rate of Zr lies within the range of the present invention. Further, the same results have been obtained by use of the composition having a Curie point 10 to 30°C lower due to substitution of part of Ti with Sn or part of Ba with Sr, Ca, Ce, without substituting $BaTiO_3$ with Zr.

Further, a multilayer ceramic capacitor formed by use of composition obtained by adding 0.25 mol MnO and CoO to the Example 3 will be described hereinbelow.

First, $BaTiO_3$ having the composition as described above and other calcined powder were weighed by a balance at predetermined proportion, mixed into slurry by adding an organic solvent and a binder, and formed into a 30 μm thick green sheet with a doctor blade casting machine. On this green sheet, a 70Ag/30Pd electrode paste was printed into a predetermined pattern and 20 sheets having the above electrode pattern were stacked and laminated. Thereafter, the laminated sheet was cut off into a predetermined shape, heated to burn out the binder and sintered at 1080°C for 2 H. After sintering, an Ag paste was baked as external lectrodes to manufacture multilayer c ramic capacitors. The electric characteristics are listed in Table 3 below.

Table 4

Shape	1.6x3.2x0.9 (mm^3)
Thickness per layer	20 (μm)
Capacitance	76 (μF)
Dielectric Loss (Dissipation Factor)	1.1 (%)
Insulation resistance	4.3×10^5 (Mohm)
CR product (25°C)	33000 (ohmF)
(125°C)	7800 (ohmF)
Capacitance change with reference to 25°C (-55°C)	-5.8 %
(125°C)	-3.2 %

The dielectric constant of the obtained multilayer ceramic capacitor was about 2700. Table 4 indicates that the characteristics are sufficiently excellent. In particular, the temperature characteristics lie within ±7.5% or less between -55 and +125°C, which satisfies X7S 45 characteristics in EIA Standards.

As described above, since the method of manufacturing high dielectric constant ceramic material of the present invention can provide high dielectric constant ceramic composition excellent in various characteristics such that the dielectric constant is high and dielectric constant change rate is small over a wide temperature range, the method is effective in manufacturing multilayer ceramic capacitors, in particular. Further, in the manufacturing method of the present invention, lead zinc niobate and barium titanate have been used as the main components; however, there exist some cases where the similar effects as those in the present invention can be obtained by use of other components.

According to the ceramic omposition and the method of the present invention, it is possible to obtain a high dielectric constant ceramic material having high insulation resistance and excellent temperature characteristics. In particular, since it is possible to obtain ceramics improving the temperature characteristics over a wide temperature range the ceramic material of the present invention is well applied to multilayer ceramic elements such as multilayer ceramic capacitors, multilayer ceramic displacement element, etc.

Claims

1. A high dielectric constant ceramic material, comprising a composition expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

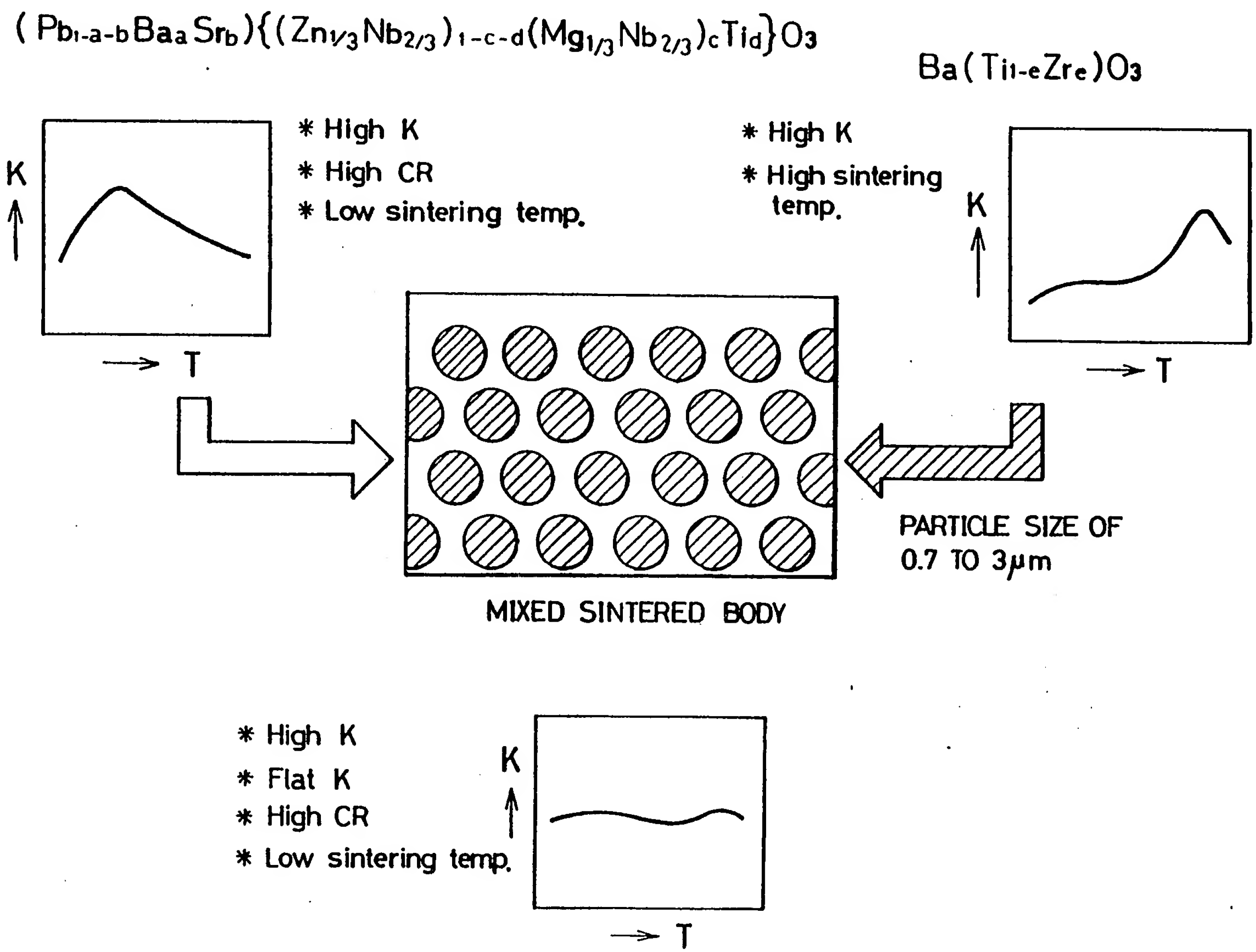
$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$

(e) baking Ag paste or Ag/Pd paste onto the sintered body as an external electrode to fabricate a ceramic capacitor.

FIG.3



$(Pb_{1-a-b}Ba_aSr_b)\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3$
K
T
* High K
* High CR
* Low sintering temp.
$Ba(Ti_{1-e}Zr_e)O_3$
* High K
* High sintering temp.
K
T
PARTICLE SIZE OF 0.7 TO 3μm
MIXED SINTERED BODY
* High K
* Flat K
* High CR
* Low sintering temp.
K
T

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(54) High dielectric constant ceramic material and method of manufacturing the same.

(57) A ceramic material comprising a composition expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$
$0 < d \leq 0.5$
$0 < c+d < 1.0$
$0.3 \leq x \leq 0.65$

having a high dielectric constant (K = 2300 to 7000), a high insulation resistance (CR = 4000 to 18000 ohmF), a low temperature dependence (±10%) to (±22, -33%) upon dielectric constant over a wide temperature range (-55 and +125°C) and a relatively low sintering temperature (1000°C to 1250°C) is disclosed. It is manufactured when $BaTiO_3$ powder (at least 50 wt% of which is 0.7 to 3 µm in particle size) is mixed with another compound with perovskite structure mainly composed of oxides of Pb, Ba, Sr, Zn, Nb, Mg and Ti before sintering. Further, part of Ti of $BaTiO_3$ is substitutable with Zr or Sn, and part of Ba of $BaTiO_3$ is sustitutable with Sr, Ca or Ce.

EP 0 257 653 A3

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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 2546

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,X	CHEMICAL ABSTRACTS, vol. 107, no. 2, 8th November 1986, abstract no. 16348h, Columbus, Ohio, US; & JP-A-61 251 563 (TOSHIBA CORP.) 30-05-1985 * Abstract * -----	1,12	C 04 B 35/46 H 01 G 4/12 H 01 B 3/12
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 04 B 35/00 H 01 G 4/12

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-04-1989	DROUOT M.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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FIG.1

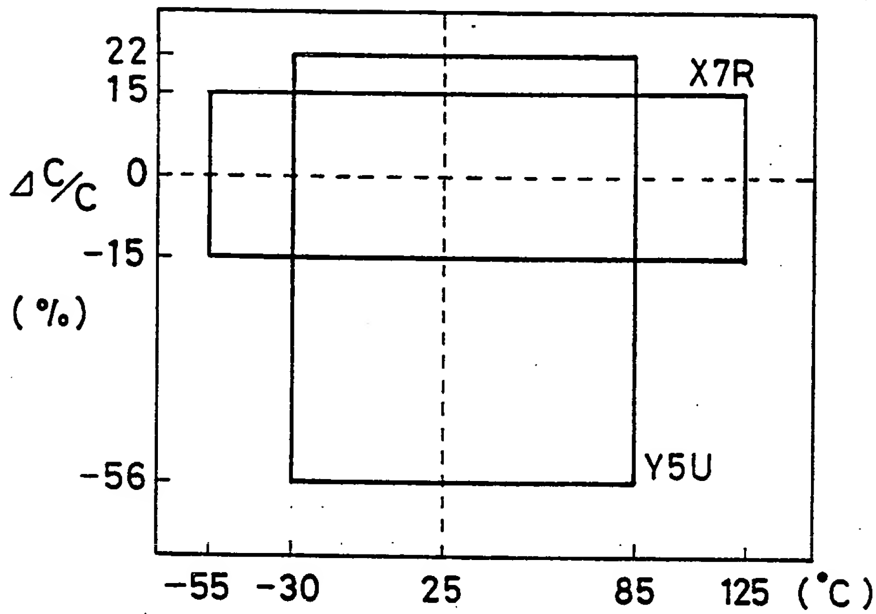
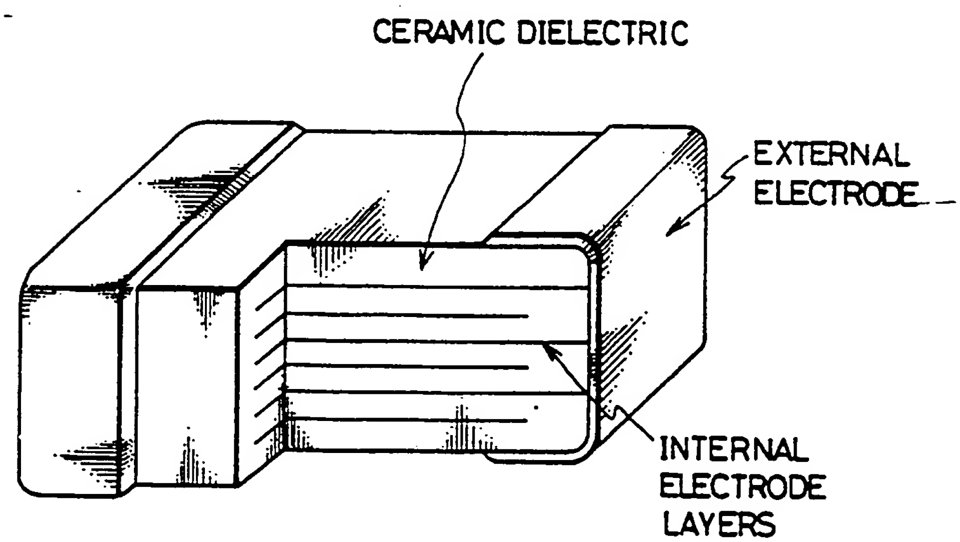


FIG.2
(Prior Art)



$0 < d \leq 0.5$
$0 < c+d < 1.0$
$0.3 \leq x \leq 0.65$

2. The high dielectric constant ceramic material as set forth in claim 1, wherein at least 50 wt% $BaTiO_3$ is 0.7 to 3 μm in particle size.

3. The high dielectric constant ceramic material as set forth in claim 1, wherein $0.3 \leq x \leq 0.5$ and $0 < c \leq 0.9$ for providing a lower sintering temperature.

4. The high dielectric constant ceramic material as set forth in claim 1, wherein $0.5 \leq x \leq 0.65$ for providing a smaller temperature dependence upon dielectric constant.

5. The high dielectric constant ceramic material as set forth in claim 1, wherein part of Ti of $BaTiO_3$ is substituted for by Zr as expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBa(Ti_{l-e}Zr_e)O_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$
$0 < d \leq 0.5$
$0 < e \leq 0.06$
$0.3 \leq x \leq 0.65$
$0 < c+d < 1.0$

6. The high dielectric constant ceramic material as set forth in claim 5, wherein $0.3 \leq x\ 0.5$ and $0 < c \leq 0.9$ for providing a lower sintering temperature.

7. The high dielectric constant ceramic material as set forth in claim 5, wherein $0.5 \leq x \leq 0.65$ for providing a smaller temperature dependence upon dielectric constant.

8. The high dielectric constant ceramic material as set forth in claim 1, wherein part of Ti of $BaTiO_3$ is substituted for by Sn.

9. The high dielectric constant ceramic material as set forth in claim 1, wherein part of Ba of $BaTiO_3$ is substituted for by Sr.

10. The high dielectric constant ceramic material as set forth in claim 1, wherein part of Ba of $BaTiO_3$ is substituted for by Ca.

11. The high dielectric constant ceramic material as set forth in claim 1, wherein part of Ba of $BaTiO_3$ is substituted for by Ce.

12. A method of manufacturing a high dielectric constant ceramic material, which comprises the following steps of:

(a) weighing $BaCO_3$ and TiO_2 at a ratio in order that barium titanate can be formed;
(b) mixing and calcining the weighed $BaCO_3$ and TiO_2 at 1000 to 1350°C;
(c) crushing the calcined barium titanate in such a way that at least 50 wt% of the barium titanate is 0.7 to 3 μm in particle size, to obtain a first compound based on barium titanate;
(d) weighing oxides of Pb, Ba, Sr, Zn, Nb, Mg, and Ti at a predetermined mixture ratio;
(e) mixing and calcining the weighed oxides at 700 to 900°C;
(f) crushing the calcined oxides into powder having particle size smaller than 0.7 μm, to obtain a second compound of lead perovskite relaxor with perovskite structure with a Curie point of 125°C or lower;
(g) weighing the first and second compounds at a predetermined ratio;
(h) mixing the weighed first and second compounds;
(i) forming the mixed compound into a predetermined shape; and
(j) sintering the formed composition at a low temperature from 1000 to 1250°C.

13. The method of manufacturing a high dielectric constant ceramic material as set forth in claim 12, which further comprises the following steps of:

(a) adding a binder and a solvent to the mixed composition into a slurry;
(b) casting to form a green sheet;
(c) printing 70Ag/30Pd to 70Pd/30Ag electrode paste on the formed gr en sheet;
(d) stacking and laminating the green sheets before sintering;

Table 3

Shape	1.6x3.2x0.9 (mm^3)
Thickness per layer	20 (μm)
Capacitance	0.17 (μF)
Dielectric Loss (Dissipation Factor)	1.0 (%)
Insulation resistance	1.9×10^5 (Mohm)
CR product (25°C)	32000 (ohmF)
(125°C)	7400 (ohmF)
Capacitance change with reference to 25°C (-55°C)	-20 %
(125°C)	+ 8 %

The dielectric constant of the obtained multilayer ceramic capacitor was about 5700. Table 3 indicates that the characteristics are sufficiently excellent. In particular, the temperature characteristics lie within ±22% or less between -55 and +125°C, which satisfies X7S characteristics in EIA Standards.

Further, a multilayer ceramic capacitor formed by use of composition obtained by adding 0.1 mol MnO and CoO to the Example 15 will be described hereinbelow.

First, $BaTi_{0.95}Zr_{0.05}O_3$ having the composition as described above and other calcined powder were weighed by a balance at predetermined proportion, mixed into slurry by adding an organic solvent and a binder, and formed into a 30 μm thick green sheet with a doctor blade casting machine. On this green sheet, a 70Pd/30Ag electrode paste was printed into a predetermined pattern and 20 sheets having the above electrode pattern were stacked and laminated. Thereafter, the laminated sheet was cut off into a predetermined shape, heated to burn out the binder and sintered at 1220°C for 2 H. After sintering, an Ag paste was baked as external electrodes to manufacture multilayer ceramic capacitors. The electric characteristics are listed in Table 4 below.

or

$$(Pb_{(1-x)(1-a-b)}\,Ba_{(1-x)a+x}Sr_{(1-x)b})\{(Zn_{1/3}Nb_{2/3})_{(1-x)(1-c-d)}$$

$$(Mg_{1/3}\,Nb_{2/3})_{(1-x)c}Ti_{(1-x)d+x(1-e)}Zr_{x.e}\}O_3)$$

which includes $Ba(Ti_{1-e}Zr_e)O_3$ having a Curie point 10 to 30 degrees lower than that of pure $BaTiO_3$, together with Comparative Example 5.

Table 2-a

Sample No.	a (mol%)	b (mol%)	c (mol%)	d (mol%)	e (mol%)	x (mol%)
Example 13	30	0	80	5	5	60
" 14	0	30	10	40	50	55
" 15	20	0	0	30	5	58
Compara. 5	0	30	10	40	12	55

Table 2-b

Sample No.	PbO (wt%)	BaO (wt%)	SrO (wt%)	ZnO (wt%)	MgO (wt%)	Nb_2O_5 (wt%)	TiO_2 (wt%)	ZrO_2 (wt%)
Example 13	23.73	41.93	0.00	0.62	1.63	12.79	17.90	1.40
" 14	27.17	32.59	5.41	2.36	0.23	9.24	21.69	1.31
" 15	27.93	37.92	0.00	2.97	0.00	9.70	20.15	1.33
Compara 5	26.99	32.38	5.37	2.34	0.23	9.19	20.37	23.12

Table 1-b

Sample No.	PbO (wt%)	BaO (wt%)	SrO (wt%)	ZnO (wt%)	MgO (wt%)	Nb_2O_5 (wt%)	TiO_2 (wt%)
Example 1	41.97	18.94	4.28	4.98	0.03	16.46	13.35
" 2	32.96	33.69	0.00	2.99	0.03	9.96	20.37
" 3	43.90	21.17	1.07	3.37	1.11	18.35	11.03
" 4	45.82	21.20	0.21	1.12	2.23	18.37	11.05
" 5	35.96	30.21	0.00	2.43	1.20	15.87	14.31
Compara. 1	32.96	33.69	0.00	2.99	0.03	9.96	20.37
" 2	32.96	33.69	0.00	2.99	0.03	9.96	20.37
Example 6	39.74	22.59	3.98	2.17	1.08	14.18	16.27
" 7	28.06	38.10	0.00	2.98	0.00	9.75	21.00
" 8	28.16	37.03	0.82	2.99	0.02	9.92	21.06
" 9	25.70	40.43	0.00	2.73	0.00	8.93	22.21
" 10	29.79	36.39	0.00	3.17	0.00	10.35	20.30
" 11	30.17	32.96	2.63	3.21	0.00	10.48	20.55
" 12	27.39	39.99	0.00	0.21	1.03	7.48	23.90
Compara. 3	29.79	36.39	0.00	3.17	0.00	10.35	20.30
" 4	29.79	36.39	0.00	3.17	0.00	10.35	20.30

In this case, particle size of $BaTiO_3$ powder thus obtained was controlled by modifying the crushing conditions of the ball mill. Further, mean particle size was measured in accordance with Blaine method with a Blaine air permeability apparatus prescribed in Testing Method of Japanese Industrial Standard R-5201-1964.

On the other hand, oxides or hydrooxides or carbonates of Pb, Ba, Sr, Zn, Ti, Mg, etc. other than $BaTiO_3$ were mixed by another ball mill, calcined at 700 to 900°C, and crushed.

Succeedingly, these calcined bodies were weighed by a balance so as to provide a predetermined proportion, and mixed in a pot mill. After drying, a binder was mixed to form granule, and the material was pressed to form a disk-shaped element with a diameter of 17 mm and a thickness of about 2 mm.

The element was sintered in air at 1000 to 1250°C for 2 hours. (Examples 1 to 6 and Comparative Examples 1 to 2 were sintered at 1000 to 1100°C, while Examples 7 to 15 and Comparative Examples 3 to 5 were sintered at 1200 to 1250°C.) Silver electrodes were baked onto both the main surfaces to measure various characteristics. The dielectric loss (dissipation factor) and the capacitance were measured by an LCR meter at 1 kHz, 1 Vrms, and 25°C. The dielectric constants were calculated on the basis of these values. Further, the insulation resistances were calculated on the basis of values measured with an insulation resistance meter after a voltage of 100 V had been applied for 2 minutes. Further, the temperature characteristics (dependence) of the dielectric constant were expressed as the maximum change rate within a temperature range of -55 to +125°C with reference to 25°C. The capacitance and resistance product (CR product) was obtained on the basis of (relative dielectric constant) × (insulation resistance) × (dielectric constant in a vacuum) at 25 and 125°C. The insulation resistance was measured in a silicon oil to eliminate the moisture effect induced in air.

Table 1 shows the test results of Examples 1 to 5 and 7 to 12 having composition expressed by the general formula:

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3$$

or

$$(Pb_{(1-x)(1-a-b)}Ba_{(1-x)a+x}Sr_{(1-x)b})$$

$$\{(Zn_{1/3}Nb_{2/3})_{(1-x)(1-c-d)}(Mg_{1/3}Nb_{2/3})_{(1-x)c}Ti_{(1-x)d+x}\}O_3).$$

For comparison, Table 1 lists the test results of Comparative Example 1 ($BaTiO_3$ of small particle size), Comparative Example 2 ($BaTiO_3$ of large particle size), and a special Example 6 ($BaTiO_3$ is replaced with $(Ba_{0.9}Sr_{0.1})TiO_3$ having a Curie point 10 to 30°C lower than that of pure $BaTiO_3$).

The ceramic composition thus obtained is a mixed sintered body of a first component mainly composed of $BaTiO_3$ and a second component with perovskite structure mainly composed of Pb. Since the first compound of $BaTiO_3$ has a Curie point of about 125°C, and due to a multiplication effect in relation to the second component mainly composed of Pb, excellent temperature characteristics or small temperature dependence in the present ceramic composition can be obtained. Further, the present ceramic composition is high in dielectric constant and CR product, and therefore suitable for use in capacitors.

If the $BaTiO_3$ powder is excessively fine, first and second components are excessively diffused in sintering, thus resulting in obstruction of an improvement in temperature characteristics. If excessively coarse, pore cracks excessively increase in the sintered body, thus resulting in low CR product, low mechanical strength, and low production yield due to non-uniform composition especially when multilayer capacitors are fabricated.

Therefore, it is desirable that 50 wt% or more $BaTiO_3$ powder is 0.7 to 3 μm, preferably 0.8 to 2 μm in particle size. The method of controlling the particle size is as follows: when the particle size is large, for instance, the crushing conditions by ball mill is modified. When the particle size is small, the calcining or prefiring condition is adjusted.

Further, the Curie point of the second component is determined as 125°C or less under consideration of the temperature characteristics of $BaTiO_3$, and further as room temperature to 80°C under consideration of the mutual reaction of the first and the second components. Further, it is preferable to use the second component with a Curie point lower than room temperature when the sintering temperature is required to be lowered (e.g. 1100°C or lower).

Further, in order to change the Curie point, it is possible to substitute a part of Ba with Sr, Ca or Ce or a part of Ti with Zr or Sn in the $BaTiO_3$ powder.

The composition of the present invention will be described hereinbelow. The composition can be expressed by the following general formula

$$(1\text{-}x)(Pb_{1\text{-}a\text{-}b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1\text{-}c\text{-}d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3$$

In the above formula, only a small amount of substitution for the Pb by Ba and Sr can form a perovskite structure. However, when (a+b) is 0.01 or less, perovskite structure is not easily formed and ther fore the dielectric constant is lowered. When (a+b) is 0.35 or more, the sintering temperature increases. If c and d are out of the above ranges, the temperature dependence of the dielectric constant increases. Further, it is preferable that $(Zn_{1/3}Nb_{2/3})$ component is included to some extent, $c+d \leq 0.9$ is preferable. If x exceeds 0.65, the sintering temperature rises; if below 0.3, the temperature dependence of the dielectric constant increases. In particular, when the temperature dependence is much accounted, $0.5 < x \leq 0.65$ is preferable; when the sintered temperature is much accounted, $0.3 \leq x \leq 0.5$ is preferable.

When the constants a, b, c, d, and x are restricted within the above ranges, it is possible to obtain a ceramic composition which is large in dielectric constant, small in dielectric constant temperature dependence over a wide temperature range, high in insulation resistance, and, for example as low as 1150°C in sintering temperature.

As though the composition of the present invention is mainly composed of

$$(1\text{-}x)(Pb_{1\text{-}a\text{-}b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1\text{-}c\text{-}d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3.xBaTiO_3,$$

the above stoichiometric component ratios are not so severe.

The above oxides can be calculated in terms of weight percentage as follows:

PbO	26.49 to 53.33 wt%
BaO	5.01 to 39.48 wt%
SrO	0.00 to 9.71 wt%
ZnO	0.49 to 6.86 wt%
MgO	0.00 to 3.14 wt%
Nb_2O_5	8.00 to 23.03 wt%
TiO_2	7.81 to 23.64 wt%.

More preferably,

SUMMARY OF THE INVENTION

With these problems in mind, therefore, it is the primary object of the present invention to provide a high dielectric constant ceramic material high in dielectric constant and insulation resistance, small in temperature dependence, and sinterable at low temperature, which is suitable for use in high-performance low-cost ceramic capacitors.

To achieve the above-mentioned object, a high dielectric constant ceramic material according to the present invention comprises a ceramic composition expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3).xBaTiO_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$
$0 < d \leq 0.5$
$0 < c+d < 1.0$
$0.3 \leq x \leq 0.65$

In manufacturing the above-mentioned ceramic composition, at least 50 wt% or more barium titanate ($BaTiO_3$) powder used as raw material is 0.7 to 3μm in particle size.

Further, part of Ti of $BaTiO_3$ can be substituted for by Zr as expressed by the following formula as

$$(1-x)(Pb_{1-a-b}Ba_aSr_b)$$

$$\{(Zn_{1/3}Nb_{2/3})_{1-c-d}(Mg_{1/3}Nb_{2/3})_cTi_d\}O_3).xBa(Ti_{1-e}Zr_e)O_3$$

where

$0 \leq a \leq 0.35$
$0 \leq b \leq 0.35$
$0.01 \leq a+b \leq 0.35$
$0 \leq c \leq 0.9$
$0 < d \leq 0.5$
$0 < e \leq 0.06$
$0.3 \leq x \leq 0.65$
$0 < c+d < 1.0$

Or else, part of Ti of $BaTiO_3$ can be substituted for by Sn.

Furthermore, part of Ba of $BaTiO_3$ can be substituted for by Sr, Ca or Ce.

It is the other object of the present invention to provide a method of manufacturing a high dielectric constant ceramic material provided with the above features.

To achieve the above-mentioned object, the method of manufacturing a high dielectric constant ceramic material comprises the following steps of: (a) weighing $BaCO_3$ and TiO_2 at a ratio in order that barium titanate can be formed; (b) mixing and calcining the weighed $BaCO_3$ and TiO_2 at 1000 to 1350°C; (c) crushing the calcined barium titanate in such a way that at least 50 wt% of the barium titanate is 0.7 to 3 μm in particle size, to obtain a first compound based on barium titanate; (d) weighing oxides of Pb, Ba, Sr, Zr, Nb, Mg, and Ti at a predetermined mixture ratio; (e) mixing and calcining the weighed oxides at 700 to 900°C; (f) crushing the calcined oxides into powder having particle size smaller than 0.7 μm, to obtain a second compound of lead perovskite relaxor with perovskite structure with a Curie point of 125°C or lower; (g) weighing the first and second compounds at a predetermined ratio; (h) mixing the weighed first and second compounds; (i) forming the mixed compound into a predetermined shape; and (j) sintering the formed composition at a low temperature from 1000 to 1250°C.

temperature range (-55 and +125°C) and a relatively low sintering temperature (1000°C to 1250°C) is disclosed. It is manufactured when $BaTiO_3$ powder (at least 50 wt% of which is 0.7 to 3 μm in particle size) is mixed with another compound with perovskite structure mainly composed of oxides of Pb, Ba, Sr, Zn, Nb, Mg and Ti before sintering. Further, part of Ti of $BaTiO_3$ is substitutable with Zr or Sn, and part of Ba of $BaTiO_3$ is sustitutable with Sr, Ca or Ce.